

CORRECTED  
VERSION\*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

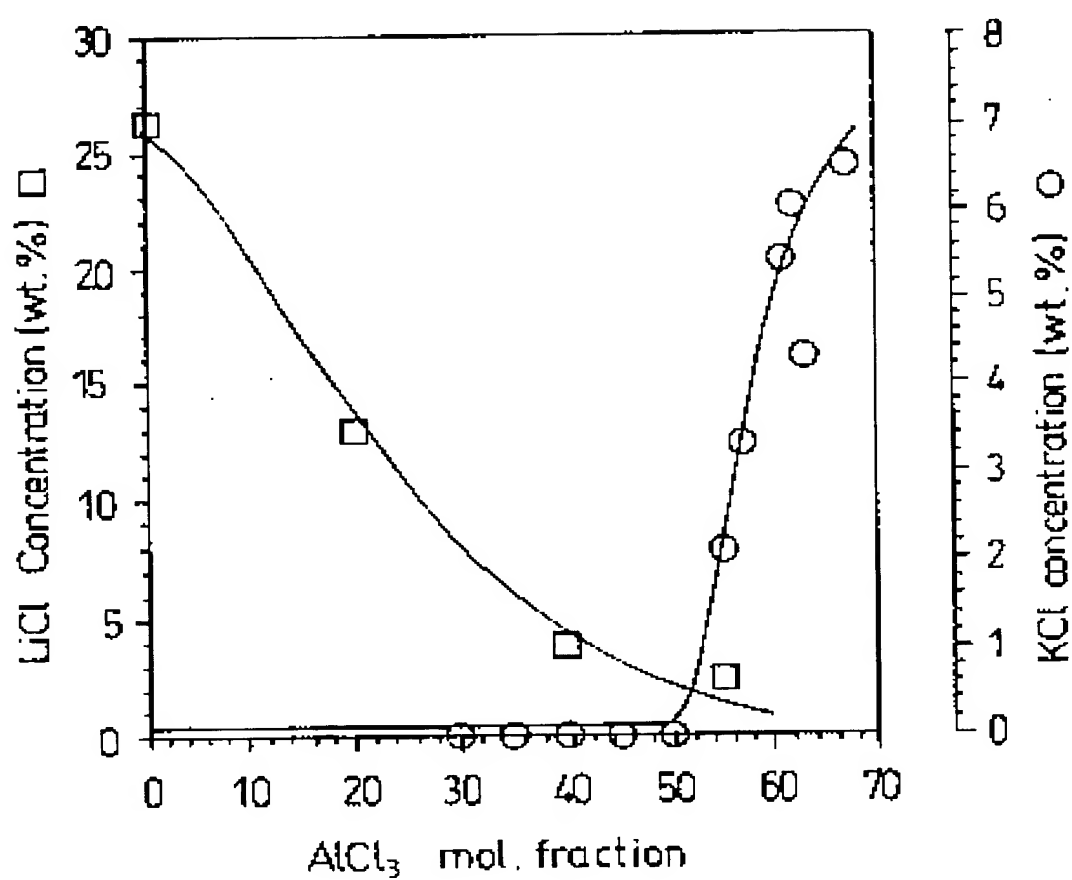
<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C01D 3/18, G21C 19/48</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/14160</b> <b>(43) International Publication Date:</b> 25 March 1999 (25.03.99)
<b>(21) International Application Number:</b> PCT/GB98/02743 <b>(22) International Filing Date:</b> 16 September 1998 (16.09.98)  <b>(30) Priority Data:</b> 9719551.5 16 September 1997 (16.09.97) GB  <b>(71) Applicant (for all designated States except US):</b> BRITISH NUCLEAR FUELS PLC [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> FIELDS, Mark [GB/GB]; 22 Abbey Heights, Ireleth, Askam-in-Furness, Cumbria CA16 7HT (GB). THIED, Robert, Charles [GB/GB]; BNFL, Sellafield, Seascale, Cumbria CA20 1PG (GB). SEDDON, Kenneth, Richard [GB/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB). PITNER, William, Robert [US/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB). ROONEY, David, William [IE/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB).  <b>(74) Agent:</b> HARRISON GODDARD FOOTE; Belmont House, 20 Wood Lane, Leeds LS6 2AE (GB).		<b>(81) Designated States:</b> CA, CN, JP, KR, RU, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TREATMENT OF MOLTEN SALT REPROCESSING WASTES  <b>(57) Abstract</b> <p>A method of removing from a metal salt ionic species contained therein involves contacting the metal salt with an ionic liquid to dissolve the metal salt, the ionic species or both. At least in the case where both the metal salt and the ionic species are dissolved, the resultant ionic liquid composition is treated to separate the ionic species therefrom and subsequently processed to recover the metal salt.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

1/6

*Fig. 1*

2/6

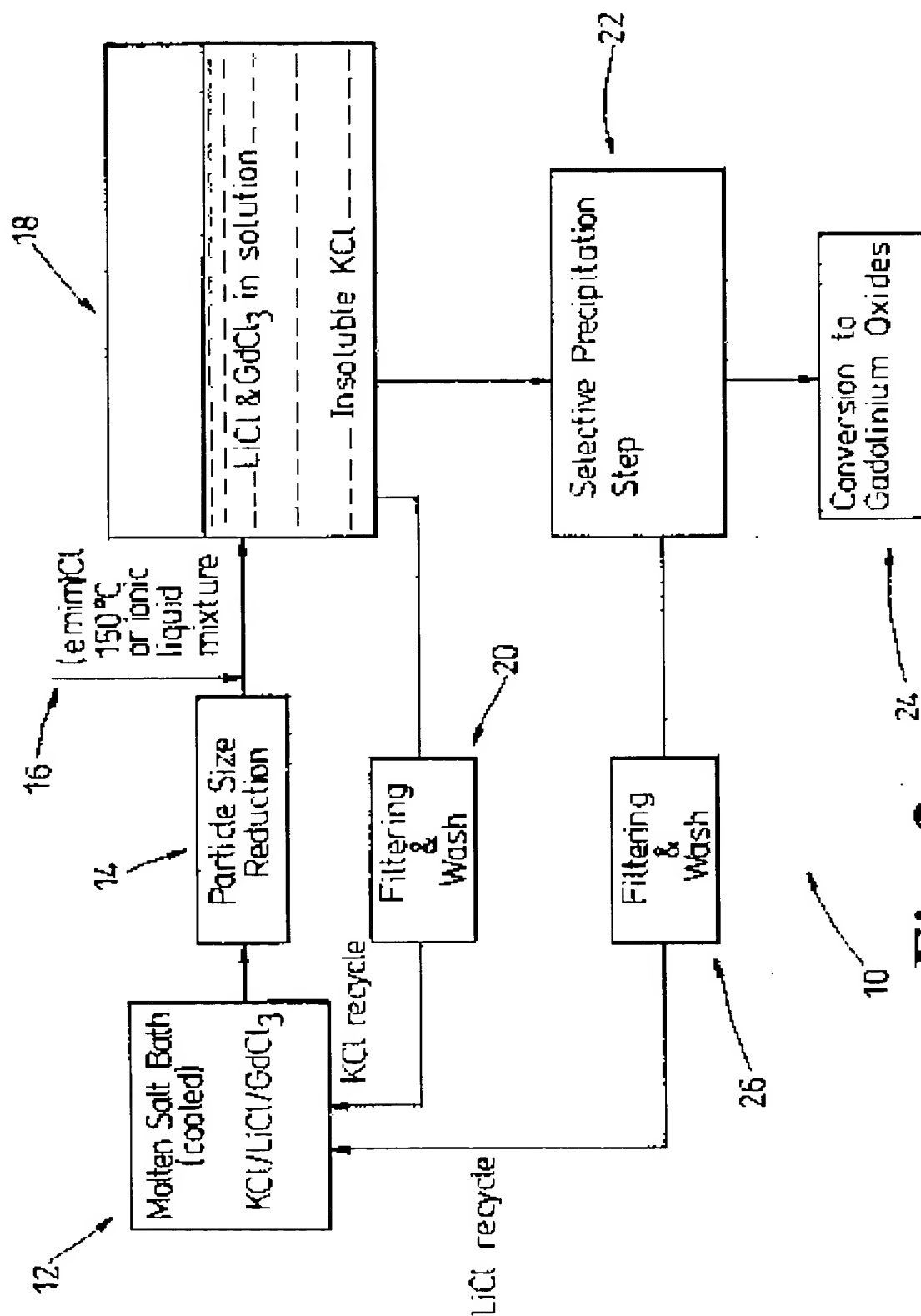
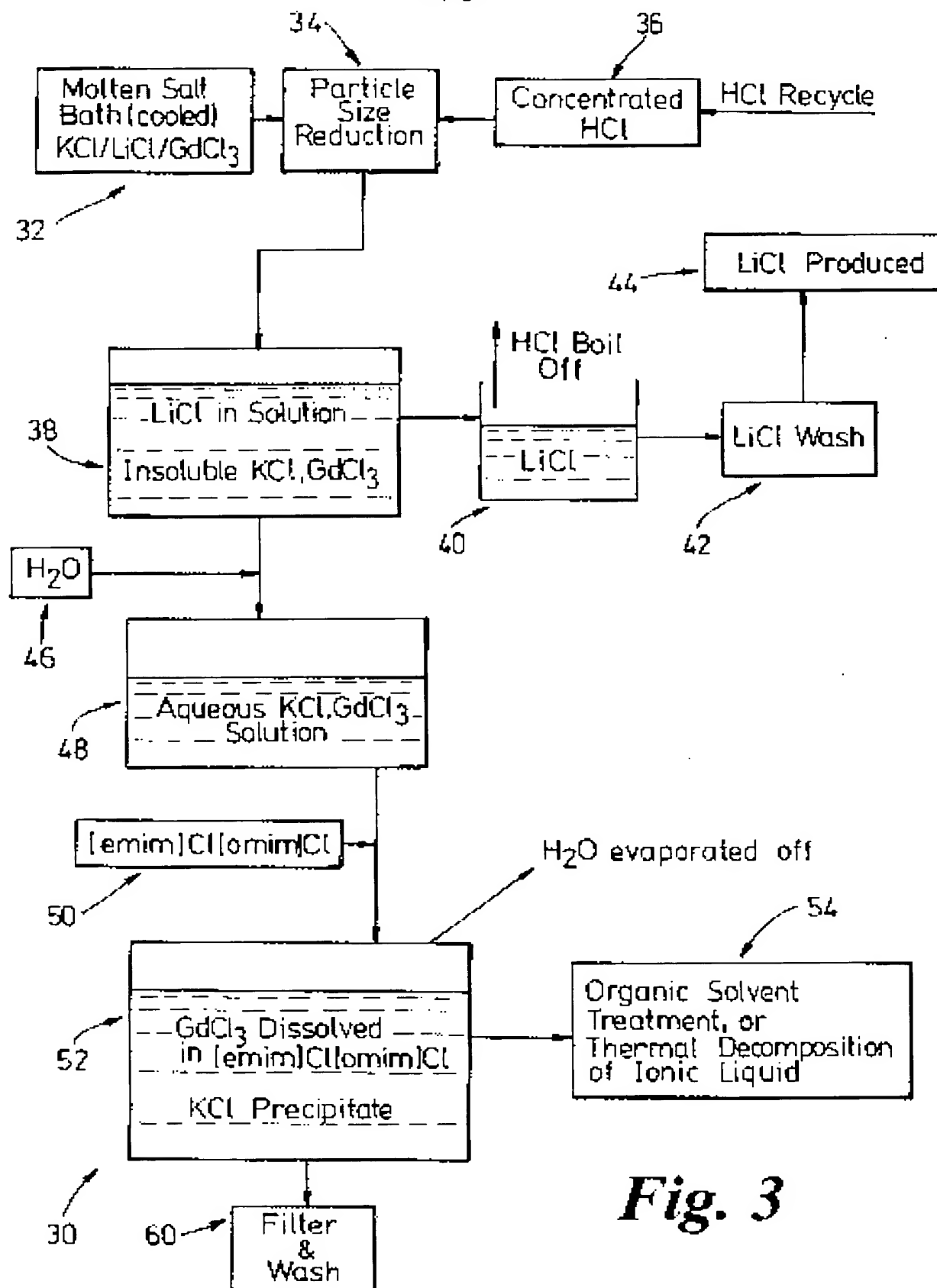
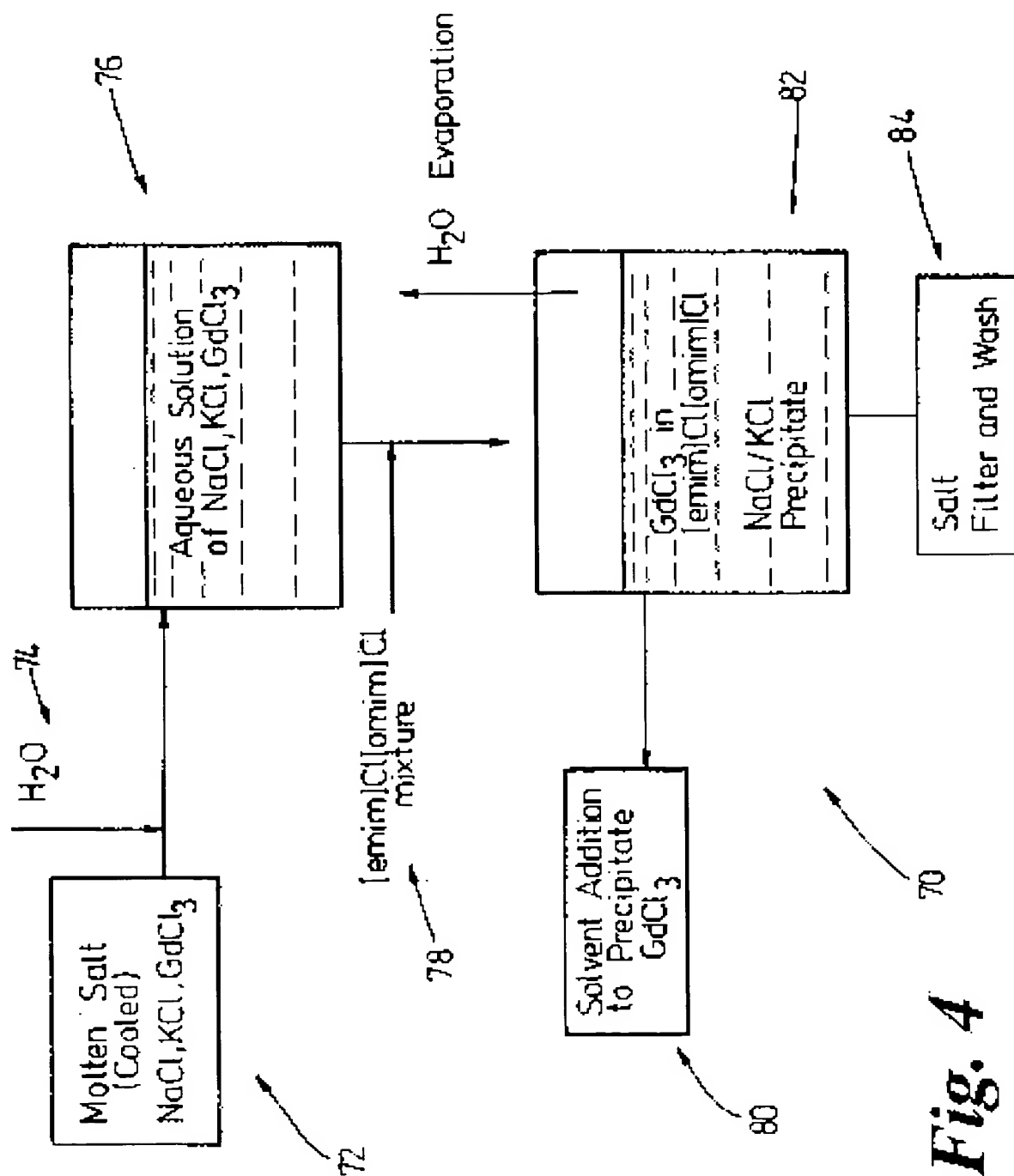


Fig. 2

3/6

**Fig. 3**

4/6

**Fig. 4**

5/6

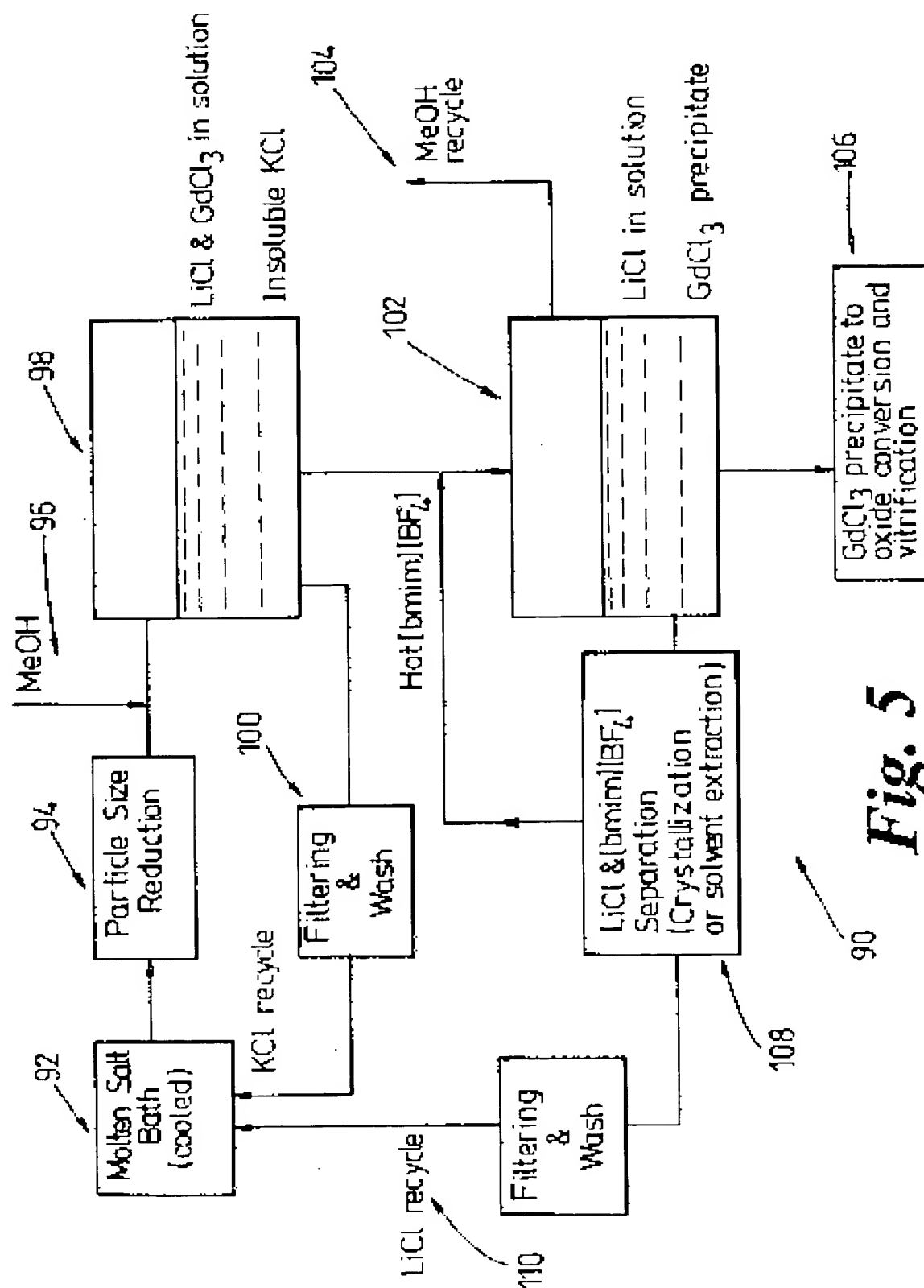
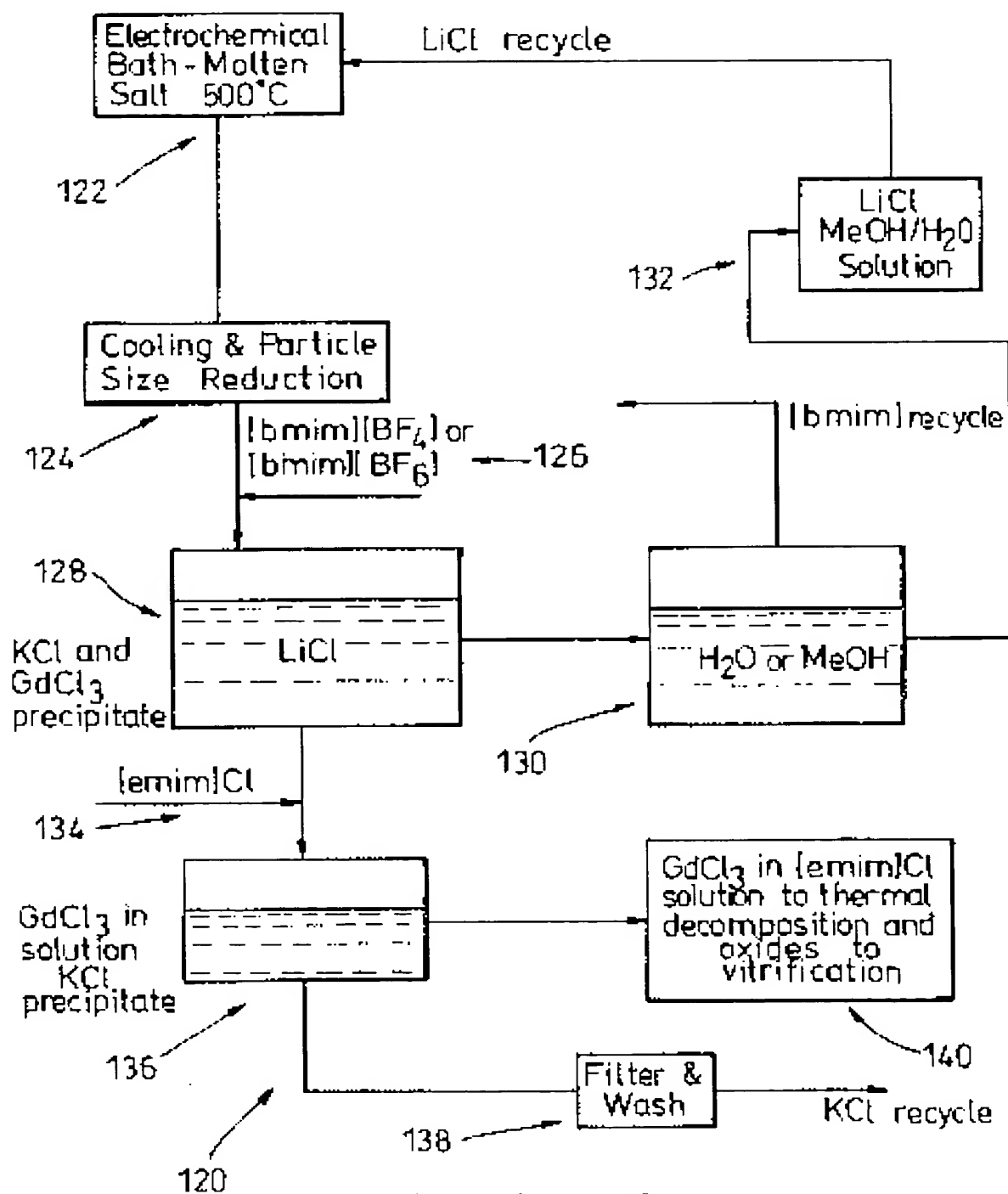


Fig. 5

6/6

**Fig. 6**



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number  
**WO 01/15175 A2**

(51) International Patent Classification<sup>7</sup>: **G21F 9/00**

(21) International Application Number: PCT/GB00/03234

(22) International Filing Date: 21 August 2000 (21.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
9919606.5 19 August 1999 (19.08.1999) GB

(71) Applicant (for all designated States except US): **BRITISH NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JEAPES, A., J.** [GB/GB]; British Nuclear Fuels Plc, Research & Technology, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). **THIED, R., C.** [GB/GB]; British Nuclear Fuels Plc, Research & Technology, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). **SEDDON, Kenneth, Richard** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast B79 5AG (GB). **PITNER, W., R.** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast B79 5AG (GB). **ROONEY, D., W.** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road,

Belfast B79 5AG (GB). **HATTER, Justine, E.** [GB/GB]; British Nuclear Fuels PLC, Risley, Warrington, Cheshire WA3 6AS (GB). **WELTON, T.** [GB/GB]; Department of Chemistry, Imperial College, Prince Consort Road, London (GB).

(74) Agent: **HARRISON GODDARD FOOTE**; Tower House, Merrion Way, Leeds LS2 8PA (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR RECYCLING IONIC LIQUIDS

(57) Abstract: A method for treating a spent ionic liquid composition includes heating the composition to form a partial decomposition product thereof. The product is separated from composition contaminants and the separated product is reacted with a reactant to regenerate the ionic liquid.

WO 01/15175 A2





## PROCESS FOR RECYCLING IONIC LIQUIDS

### FIELD OF THE INVENTION

This invention relates to processes for treating spent ionic liquids. Reference will be made hereinafter to ionic liquids which have been used in the reprocessing of nuclear fuels but it should be understood that the invention has application in all fields of ionic liquids technology, including applications outside the nuclear industry.

### BACKGROUND OF THE INVENTION

10 Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (24446331, 2446339, 2446350). In general terms an ionic liquid is a salt, a mixtures of salts, or a mixture of components which produce a salt or salts, which melts below or just above room temperature. (As used herein, the term "salt" means an entity comprising entirely of cationic and anionic species). Such liquids are known as "ionic liquids" although this term is sometimes used for salts which melt at relatively high temperatures. In this specification, the term "ionic liquid" refers to a salt which melts at a temperature of up to 100°C.

Co-pending patent application PCT/GB99/00246 discloses a method for reprocessing spent nuclear fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid to substantially separate fissile material from other components of irradiated fuel. Also disclosed is the subsequent treatment of the resulting ionic liquor, either by solvent extraction or electrochemical treatment to recover the dissolved uranium or plutonium.

25 In addition to fissile material spent ionic liquid also contains fission products which have been dissolved together with the uranium. Considerable effort has been focused on the development of a cost effective route for the removal of these contaminants, subsequent to the separation of the uranium from the mixture, in a form suitable for conversion into a stable waste form.



Contaminant removal may be achieved by any one or a combination of a number of different routes. Selected fission products such as plutonium can be electrochemically extracted through the application of a suitable potential. The disadvantage of this is that electrolysis is a costly process, especially when  
5 performed on an industrial scale.

Fission products may alternatively or additionally be extracted from the ionic liquid by the addition of an organic solvent. Addition of an organic species results in the precipitation of fission product compounds. The precipitate can be filtered from the  
10 ionic liquid and calcined to convert to oxide prior to a vitrification step. Cleaned ionic liquid can then be recycled to the electrorefiner.

Combustion is another option for removal of contaminants, wherein spent ionic liquid is heated to temperatures in excess of 200°C. The disadvantage of this process  
15 can be measured in economic terms: Combustion of imidazolium salts results in the production of carbon dioxide, water and a mixture of nitrogen oxides (NO<sub>x</sub>). This means that the ionic liquid cannot be recycled and is in fact destroyed.

Since one of the most significant costs in industry will be that of the requisite raw  
20 materials, any process which helps to minimise these costs through recycling is clearly a more viable option.

#### STATEMENT OF INVENTION

According to the present invention there is provided a method for treating a spent  
25 ionic liquid composition comprising an ionic liquid and contaminant, the method comprising heating said ionic liquid to form a partial decomposition product thereof, separating said product from said contaminant and reacting the separated product with a reactant to regenerate said ionic liquid.

30 When 1-methyl-3-ethylimidazolium chloride is heated under reduced pressure, the ionic liquid partially decomposes to give 1-methylimidazole, 1-ethylimidazole,



chloromethane and chloroethane. In the initial experiments the thermolysis products were left for two days at room temperature and re-acted to produce a mixture of 1,3-dimethylimidazolium chloride, 1,3-diethylimidazolium chloride, and 1-methyl-3-ethylimidazolium chloride. These results are surprising because thermal decomposition was previously considered to destroy any potential for recycling of the ionic liquid. In the light of these experiments however thermal decomposition for the cleaning of ionic liquids is now an economically viable alternative.

Preferably the decomposition product is separated together with at least one other decomposition product from the contaminants. Separation is effected by volatilisation during the heating process. In one embodiment of the invention the partial decomposition product is separated from the at least one other decomposition product by distillation.

Preferably the ionic liquid is heated under reduced pressure at or below 2mmHg at a temperature ranging from 200°C to 300°C or more preferably from 220°C to 250°C.

#### DETAILED DESCRIPTION OF THE INVENTION

Spent ionic liquid, for example 1-methyl-3-ethylimidazolium chloride, is contaminated with fission products, possibly organic radiolysis products, and will require treatment in order to recover the fission products in a form suitable for conversion into a stable waste form.

In a method according to the present invention, the ionic liquid is heated under reduced pressure to a temperature within the range of 200°C to 300°C. In a preferred embodiment 1-methyl-3-ethylimidazolium is heated at a temperature from 220°C to 250°C for 2-3 hours at pressures below 2mmHg. These conditions allow for only partial decomposition of the ionic liquid and therefore the recovery of as many useful component compounds of the ionic liquid as possible. It should be understood that the conditions for partial decomposition will vary for differently substituted imidazolium salts and for different mixtures thereof.





Thermolysis of the ionic liquid results in the evolution of volatile thermolysis products. In the case of 1-methyl-3-ethylimidazolium chloride these are 1-methylimidazole, 1-ethylimidazole, chloromethane and chloroethane. Chloroethane then decomposes to hydrogen chloride and ethene.

Volatile products can be collected in a cold trap and subsequent distillation of the mixture allows for separation of the components. The most volatile components are hydrogen chloride and ethene. Hydrogen chloride can be scrubbed from the system using a hydroxide scrubber and ethene can either be bottled or burnt as a by-product.

1-methylimidazole and 1-ethylimidazole can be separated by distillation to allow for regeneration of the specific ionic liquid 1-methyl-3-ethylimidazolium chloride. It should be understood that separation is not required for processes which operate on a mixture of 1-methyl-3-ethylimidazolium chloride, 1,3-dimethylimidazolium chloride and 1,3-diethylimidazolium chloride.

If the specific ionic liquid 1-methyl-3-ethylimidazolium chloride is required, separated 1-methylimidazole is reacted with chloroethane so as to regenerate the original ionic liquid 1-methyl-3-ethylimidazolium chloride. Because some chloroethane is lost through its decomposition, fresh chloroethane is added to fully regenerate the ionic liquid. 1-ethylimidazole is reacted with chloromethane to regenerate the ionic liquid 1-methyl-3-ethylimidazolium chloride.

In a preferred embodiment of the invention the fission product residue is calcined to convert it into a stable waste form. In an alternative embodiment fission product residue is reacted with boric acid to convert it into a suitable form for disposal.



## CLAIMS

1. A method for treating a spent ionic liquid composition comprising an ionic liquid and contaminants, the method comprising heating said ionic liquid to form a partial decomposition product thereof, separating said product from said contaminants and reacting the separated product with a reactant to regenerate said ionic liquid.  
5
2. A method according to claim 1 wherein said partial decomposition product is separated together with at least one other decomposition product from said contaminants.  
10
3. A method according to claim 2 or claim 3 wherein said partial decomposition product is separated from the at least one other decomposition product by distillation.  
15
4. A method according to any of the preceding claims wherein said partial decomposition product is reacted with at least one other decomposition product to regenerate said ionic liquid.  
20
5. A method according to any of the preceding claims wherein said separation is effected by volatilisation during the heating process.
6. A method according to any preceding claim wherein the ionic liquid is 1-methyl-3-ethylimidazolium chloride.  
25
7. A method according to claim 6 wherein the partial decomposition product is a mixture of 1-methylimidazole, 1-ethylimidazole, chloromethane and chloroethane.  
30



8. A method according to claim 7 wherein 1-methylimidazole is reacted with chloroethane to regenerate 1-methyl-3-ethylimidazolium chloride.
- 5 9. A method according to claim 5 wherein the partial decomposition product is 1-ethylimidazole.
10. A method according to claim 9 wherein 1-ethylimidazole is reacted with chloromethane to regenerate 1-methyl-3-ethylimidazolium chloride.
- 10 11. A method according to any preceding claim wherein the ionic liquid is heated under reduced pressure.
12. A method according to claim 11 wherein the pressure is at or below 2mmHg.
- 15 13. A method according to any preceding claim wherein the ionic liquid is heated to a temperature from 200 to 300°C.
14. A method according to claim 13 wherein the ionic liquid is heated to a temperature from 220 to 250°C.
- 20 15. A method according to any of claims 3 to 14 wherein volatile products resulting from volatilisation of the ionic liquid are collected in a cold trap.
- 25 16. A method according to any preceding claim wherein hydrogen chloride is produced by heating said ionic liquid and is scrubbed from the system using a hydroxide scrubber.
17. A method according to any preceding claim wherein ethene is produced by heating said ionic liquid.

30



18. A method according to claim 17 wherein said ethene is bottled or burnt as a by product.
- 5 19. A process for the reprocessing of nuclear fuel and the treatment of salt wastes contaminated with fission products, the process including a method of any preceding claim.
- 10 20. A process according to claim 19 wherein the fission product contaminant residue is separated and calcined before disposal.
21. A process according to claim 19 wherein the fission product contaminant residue is reacted with boric acid before disposal.
- 15 22. Use of thermal decomposition in the treatment of spent ionic liquids wherein the decomposition products are used in the regeneration of an ionic liquid.
23. Use according to claim 23 wherein the ionic liquid is used in the reprocessing of spent nuclear fuel.

20

PI5693





(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number  
**WO 01/15175 A3**

(51) International Patent Classification: **G21C 19/48**

(21) International Application Number: PCT/GB00/03234

(22) International Filing Date: 21 August 2000 (21.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
9919606.5 19 August 1999 (19.08.1999) GB

(71) Applicant (for all designated States except U.S.): **BRITISH NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).

(72) Inventors; and

(75) Inventors/Applicants (for U.S. only): **JEAPES, A., J.** [GB/GB]; British Nuclear Fuels Plc, Research & Technology, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). **THIED, R., C.** [GB/GB]; British Nuclear Fuels Plc, Research & Technology, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). **SEDDON, Kenneth, Richard** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast B79 5AG (GB). **PITNER, W., R.** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast B79 5AG (GB). **ROONEY, D., W.** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast B79 5AG (GB). **HATTER, Justine, E.** [GB/GB];

British Nuclear Fuels PLC, Risley, Warrington, Cheshire WA3 6AS (GB). **WELTON, T.** [GB/GB]; Department of Chemistry, Imperial College, Prince Consort Road, London (GB).

(74) Agent: **HARRISON GODDARD FOOTE**; Belgrave Hall, Belgrave Street, Leeds LS2 8DD (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

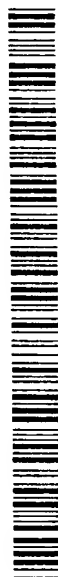
(88) Date of publication of the international search report:  
21 February 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette

(54) Title: PROCESS FOR RECYCLING IONIC LIQUIDS

(57) Abstract: A method for treating a spent ionic liquid composition includes heating the composition to form a partial decomposition product thereof. The product is separated from composition contaminants and the separated product is reacted with a reactant to regenerate the ionic liquid.

WO 01/15175 A3





# INTERNATIONAL SEARCH REPORT

National Application No  
PCT/GB 00/03234

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 G21C19/48

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document with indication, where appropriate, of the relevant passages	Relevant to claim No
P, A	WO 99 41752 A (BRITISH NUCLEAR FUELS PLC ; PITNER WILLIAM ROBERT (GB); ROONEY DAVI) 19 August 1999 (1999-08-19) the whole document ---	1
A	WO 99 14160 A (BRITISH NUCLEAR FUELS PLC ; PITNER WILLIAM ROBERT (GB); FIELDS MARK) 25 March 1999 (1999-03-25) the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

**\* Special categories of cited documents**

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

17 July 2001

Date of mailing of the international search report

24/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Brothier, J-A



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/03234

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9941752 A	19-08-1999	AU 2526799 A	30-08-1999
		CN 1290397 T	04-04-2001
		EP 1055240 A	29-11-2000
WO 9914160 A	25-03-1999	CN 1269767 T	11-10-2000
		EP 1019322 A	19-07-2000

